(19) Japanese Patent Office (JP),

(12) Publication of Laid-Open Patent Application (A),

(11) Publication Number of Patent Application: No. 2001-179167 (P2001-179167 A),

(43) Date of Publication of Application:

July 3, 2001. (H. 13)

(51) Int. Cl. 7: B05D 1/02, 7/00, H01L 21/208, 21/31, 21/316

Identification Mark:

FI: B05D 1/02, 7/00, H01L 21/208, 21/31, 21/316

Theme code (reference)

Z 4D075, H 5F045, Z 5F053, A 5F058, S

Request for Examination: Requested

Number of Claims: 6 OL

Total 8 pages

Continued on a last page.

(21) Application Number: No. Hei 11-367548,

(22) Date of Filing: December 24, 1999 (H. 11),

(71) Applicant: 000004237

NEC Corporation

5-7-1, Shiba, Minato-ku, Tokyo

(72) Inventor: Hiroshi Tanabe

5-7-1, Shiba, Minato-ku, Tokyo

c/o NEC Corporation

(74) Agent: Patent Attorney: 100096231 Kiyoshi Inagaki

Continued on a last page.

(54) [Title of the Invention]

Method for Forming Thin Film

(57) [Abstract]

[Problems to be solved] A quantity of a raw material to use is decreased by supplying a raw material on a substrate selectively beforehand, and a photolithography step and an etching step are omitted, so that simplification of a forming step is planned.

[Solution] A method for forming a thin film by which a silicon based semiconductor film, a silicon oxide based insulating film, and the like comprising the steps of forming a liquid pattern 103 by discharging and flying a fluid raw material as a droplet 102 in a predetermined direction plural times and selectively applying it over a substrate 101, forming a thin film pattern 104 by solidifying the liquid pattern 103, and forming a crystallized film 106 by irradiating the thin film 104 with a laser. Simplification of a forming step by omitting a lithography step and an etching step and a reduction of a quantity of a raw material to use are planned.

[What is Claimed is]

[Claim 1]

A method for forming a thin film characterized by comprising a step for forming a desired pattern by selectively applying a fluid raw material onto a substrate, and a step for forming a solidified pattern by solidifying the desired pattern over the substrate.

[Claim 2]

A method for forming a thin film according to Claim 1, wherein the step for forming the desired pattern includes a step for discharging and flying a droplet.

[Claim 3]

A method for forming a thin film according to Claim 1 or 2, further comprising a step

for forming an oxide film by covering over the solidified pattern, and a step for forming the solidified pattern with a desired thickness by grinding the oxide film and the solidified pattern.

[Claim 4]

A method for forming a thin film characterized by comprising a step for forming a desired pattern by selectively applying a fluid raw material onto a substrate, and a step for recrystallizing the desired pattern or making it amorphous over a substrate.

[Claim 5]

A method for forming a thin film according to Claim 4, wherein a step for forming the desired pattern including a step for discharging and flying a droplet.

[Claim 6]

A method for forming a thin film characterized by comprising a step for forming a thin film by applying a fluid raw material onto a substrate, and a step for oxidizing or nitriding the thin film.

[Detailed Description of The Invention]

[0001]

[Technical Field of the Invention] The present invention relates to a method for forming a thin film comprising a semiconductor, an insulator, a conductor, and the like over a semiconductor base substance or an insulating material base substance, especially, a manufacturing method for a thin film, and particularly relates to a method for forming a thin film which is suitable for forming a silicon based semiconductor film, a silicon oxide based insulating thin film, and the like over a semiconductor substrate or a glass substrate.

[0002]

[Conventional Art] A semiconductor element which is spread widely until now, for example, a silicon based MOS device, has an active layer inside a silicon wafer and forms a MOS (Metal-Oxide-Semiconductor) structure by forming a gate electrode over a surface oxidized film which has been thermally oxidized. Inside the silicon wafer, an impurity diffusion layer is locally controlled by using an ion implantation method or the like, and there are few examples using a local structural change such as an island-like structure. On the other hand, since a gate electrode, a metal wiring, and the like which are formed over a silicon wafer need signal transmission between the desired elements, they are formed in a predetermined pattern shape such as a linear shape or an island-like shape. Generally, such a pattern formation is performed by the following procedure.

[0003] 1) A desired thin film is formed over the entire surface of a substrate, 2) a photoresist is applied to the surface, 3) a desired area is exposed by using a stepper, 4) the exposed area is developed to form a photoresist pattern, 5) a part of the thin film which is exposed at an opening part is etched by using the photoresist pattern as a mask, 6) the photoresist is separated and cleaned.

[0004] By the above method, for example, an unnecessary part of a metal thin film which is formed over the entire surface of the substrate is selectively removed by a photolithography step and an etching step, which cause problems such as so not only a material is wasted, but also a problem such as the number of steps in addition to waste of material are increased is included. As for a means to solve these problems, a technique which the metal thin film is formed locally by a laser CVD method using an organic metal material, or the like is tried.

[0005] Further, not only the above mentioned wiring metal material, but also a patternizing of a silicon semiconductor layer which becomes an active layer has become

necessary, in addition to a rise of SOI (semiconductor-oxide film-insulator) device and a practical use of a large area device typified by an active-matrix liquid crystal display. For example, as for an amorphous silicon thin film transistor which is used in an active-matrix liquid crystal display, the steps of 1) forming an amorphous silicon nitride by a plasma-CVD method using a silane gas as a raw material, and an amorphous silicon film over the surface of the substrate, 2) applying the photoresist to the surface, 3) exposing a desired area by using a stepper, 5) developing an exposed area and forming a photoresist pattern, 6) etching the amorphous silicon thin film which is exposed at an opening part by using the photoresist pattern as a mask, 7) separating the photoresist and cleaning sequentially.

[0006] The above mentioned steps are also for selectively removing the unnecessary part by the photolithography step and the etching step, and have the same problems such as waste of materials and increase in the number of the steps as the wiring material which is already mentioned. Moreover, while as for multiple chips of the above mentioned semiconductor element are produced from a substrate of about 6 inches, even a single display device has a size such as 20 inches of a diagonal line, so the amount of the thin film which is discarded by the removal also increases exponentially.

[0007]

[Problem to be Solved by the Invention] As for a means to solve the above problems, in the Japanese Patent Laid-Open No. 4-180624, a technique by which after recrystallizing a desired pattern area of an amorphous silicon thin film, only an amorphous silicon area is etched by using difference in the etching rate of an amorphous silicon and a crystalline silicon to form a pattern which consists of crystalline silicon is proposed. By adopting such a method, there is an advantage that a photoresist process can be

omitted; however, since after a silicon system thin film is formed to an entire surface and then removed, the problem that a raw material is consumed excessively still remains.

[0008] Therefore, it is an object of the present invention to provide a method for forming a thin film which can reduce the amount of the raw material to be used together with omitting a photolithography step and an etching step.

[0009] It is another object of the present invention to provide a method for forming a new semiconductor element and a new liquid crystal element by applying a common technique to form both an insulating thin film and a conductive thin film.

[0010]

[Means to Solve the Problem] In order to achieve the above mentioned objects, the present invention provides following first to third methods for forming a thin film.

[0011] 1) A method for forming a thin film characterized by having a step which forms a desired pattern by applying a fluid raw material on a substrate selectively, and a step which forms a solidified pattern by solidifying the desired pattern over the substrate.

[0012] In the above mentioned first invention method, the desired pattern of a liquid raw material is formed by for example, applying a liquid raw material to the substrate selectively by discharging and flying a glob of a liquid raw material in a predetermined direction plural times. Hereby, a lithography step and an etching step are omitted. As for the above mentioned discharge and flight of the glob, it is desirable to simultaneously discharge a plurality of droplets selectively by using a droplet discharge means including a plurality of discharge ports which discharge a liquid raw material in the predetermined direction and a supply port of the liquid raw material. For the droplet discharge means, one which uses a vaporization and volumetric expansion

phenomenon by heating the liquid raw material, and one which uses a mechanical vibration by a piezoelectric element, or the like can be used.

[0013] As the fluid raw material, a mixture of a liquid and a particle, a particle whose fluidity is high, and the like can be used other than the above liquids. After applying, in order not to break up the pattern which is formed before a solidification step, it is necessary to adjust liquid surface tension over the substrate and viscosity appropriately. In the case where a solid state particle is used, pattern break can be prevented by charging the substrate and the solid state particle beforehand.

[0014] As for a film thickness of a thin film pattern which is formed, for example, it is desirable to control the thickness to about 1 μm. In order to obtain a desirable film thickness and a pattern size by the discharge and the flight of the droplet, conditions such as the size of the discharge port, discharge pressure, and transfer speed of the substrate or a discharge means are controlled appropriately. After forming the thin film which is thicker than a predetermined film thickness, the thickness can also be made smaller by polishing, ion milling, and the like. Moreover, in a solidification step, drying of the liquid raw material by heat, melt-solidification of the particle, solid state formation by a chemical reaction, and the like can be used.

[0015] 2) A method for forming a thin film characterized by comprising a step for forming a desired pattern by applying a fluid raw material on a substrate selectively, and a step for recrystallizing or making the desired pattern an amorphous over a substrate.

[0016] Also in the above mentioned second invention method, the discharge and the flight of the droplet can be used. In a suitable mode in the present invention, the liquid raw material is solidified on the substrate to form amorphous thin film and a polycrystalline thin film. A melt-recrystallization is promoted and crystallization of

the amorphous thin film, quality improvement and single crystallization of the polycrystalline thin film can be realized by irradiating the thin film with an energy beam such as a laser, an electron beam and a lamp light.

[0017] A method for forming the thin film characterized by comprising a step for forming a liquid pattern by applying a liquid raw material on a substrate, and a step for oxidizing or nitriding the liquid pattern.

[0018] As for applying the liquid raw material, the liquid raw material can be applied to the entire surface of the substrate or to the desired pattern by the first or the second invention method. If a high silane which is represented by a general formula Si_nH_{2n+1} (n>=2) is used as the liquid raw material, a silicon thin film with high purity is easy to obtain. In particular, a trisilane Si_3H_8, a tetrasilane Si_4H_{10}, and higher silane are easy to treat because they are liquid at a room temperature. Silanes easily react with oxygen in the atmosphere or an oxidizing atmosphere, in other words, they have a characteristic of being oxidized easily, therefore, a silicon oxide film is formed by exposing the oxidizing atmosphere after applying the high silane. After the application by using the method such as spin coating, an oxide film can be formed over the entire surface of the substrate; alternatively the oxide film is selectively formed by oxidation after selective application of the droplet.

[0019]

[Embodiment of the invention] With reference to Figs. 1 to 4, the present invention is further explained in detail based on Embodiments of the present invention. Figs. 1(a) to 1(d) are sectional views which show steps of the method for forming a thin film in an example of an embodiment of the present invention sequentially. First, a droplet 102 is flied and adhered over a substrate 101 (the same figure (a)) and then a liquid pattern 103

is formed (the same figure (b)). The pattern size and the film thickness are controlled by the unit quantity and the number of the droplets which are flied and adhered. A desired liquid pattern can be formed on a surface of the substrate 101 by transferring a droplet discharge means relatively to the substrate 101 or transferring the substrate 101 relatively to the droplet discharge means. The thin film 104 is formed by heating and drying the liquid pattern which is formed in this way (the same figure (c)). Further, a crystallized film 106 is formed by irradiating the entire surface or a part of the substrate with a laser 105 as necessary (the same figure (d)).

[0020] If a high silane which is represented by a general formula Si_nH_{2n+1} (n>=2) is used as a liquid which is used in the present embodiment, a silicon thin film with high purity is easy to obtain. In particular, a trisilane Si_3H_8, a tetrasilane Si_4H_{10}, and higher silane are easy to treat because they are liquid at a room temperature. However, it is desirable that the formation of the above mentioned droplet is performed in a nitrogen, an inert gas atmosphere, or a reduced pressure atmosphere because it is easy to react with oxygen in the atmosphere or an oxidizing atmosphere. In the step for solidifying the liquid pattern by heating using high silane, it is solidified by releasing a hydrogen atom which is combined with a silicon atom and combining silicon atoms with each other disorderly. If a heating / cooling step at about 600 °C or more in which a solid phase growth is observed within a limited time is used, a crystalline silicon thin film will be obtained because they are combined under more steady combination state. On the other hand, in the case that a glass substrate such as a liquid crystal display substrate, a treatment temperature is needed to be controlled at around 600 to 300 °C or less than that and if a heat treatment at less than around 300 °C is used, amorphous silicon is formed. In order to form the crystalline silicon thin film by a low-temperature heat

treatment, a laser recrystallization step which uses an excimer laser (XeCl, KrF, XeF, ArF, etc.), a YAG laser, an Ar laser, or the like is applied. In this case, even in the case where a low softening point substrate such as glass is used, a crystallization of the amorphous silicon can be promoted.

[0021] Fig. 2 is a drawing which shows a droplet discharge means. Fig 2(a) shows a sectional view of a single body of a discharge means. A raw material is supplied to a nozzle 201 from a supply port 204 side. For example, in the case where a tetrasilane Si_4H_{10} is used, since the boiling point under 1 atmospheric pressure is about 108 °C, a tetrasilane is vaporized and the volumetric expanded in an area near a heater in the nozzle by heating a heater 202 to about 120 °C. Since a liquid can flow out without resistance on a discharge port 203 side a liquid tetrasilane which is near the discharge port discharges and flies by the pressure of vaporization and volumetric/cubical expansion. By arranging a plurality of such above mentioned nozzles, the droplet is supplied with a high speed. Fig. 2(b) is a perspective view of the droplet discharge means having such a structure. A drive circuit 206 which controls heating of the heater 202 is connected to a control means 208, and they are held at a drive circuit substrate 205. In addition, although the nozzle 201 is arranged in the shape of one-dimensional array in the drawing, the treatment can also be performed with higher speed by arranging a nozzle array in two dimensions.

[0022] As for a droplet formation means, not only the method using the vaporization and cubical expansion mechanism by the heating which is shown in Fig. 2, but also a spouting mechanism by mechanical pressure using a piezoelectric element, or the like screen printing and an intaglio printing can be used. A silicon thin film and a silicon oxide thin film can be formed by using a silicon particle, a silicon oxide particle or one

in which they are dispersed in a solvent as a fluid raw material. In such a case, an electrostatic latent image is formed on the substrate and it is developed by using a raw material which is charged with electricity. Alternatively, the method by which the particle pattern is transferred on the substrate after developing the electrostatic latent image which is formed on a photo conductor by using the above mentioned particle may be used.

[0023] A liquid pattern formation device is schematically shown in Fig. 3. A substrate 310 where a thin film pattern should be formed is introduced in a transportation chamber 305 through a gate valve 306. As for the transportation, a transportation robot which is not illustrated is used. After introducing the substrate 310, the atmosphere inside the transportation chamber 305 is substituted by a nitrogen atmosphere. After the substitution, the substrate 310 is further introduced in a process chamber 309 through a second gate valve 306. The substrate 310 is arranged on a substrate stage 310 in the process chamber 309. The process chamber 309 is connected to an vent 312 through a third gate valve and cleaning of the atmosphere is attempted by concurrently controlling the process chamber 309 and a nitrogen introduction mechanism or an inert gas introduction mechanism (not shown). A desired pattern is formed on the substrate by moving a discharge device 308 with an appropriate gap kept on the substrate. Furthermore, the process room has a laser introduction window 307.

Reformulation or crystallization of a patterned thin film is performed by introducing laser light which is supplied from a laser oscillator 301 through an optical element 302 to a surface of the substrate 310. Also as for the laser light, it is applied to the entire surface by providing a moving means 303 in an optical element group. Although it is not illustrated, as for a laser light, one in which a spatial intensity is uniformed by using

a beam homogenizer etc. and one in which has the desired beam pattern by using a mask etc. may be accepted.

[0024] Fig. 4 shows a plan view showing the case where the liquid pattern formation device of the above mentioned embodiment is combined with another process device. A load / unload chamber C1, a plasma CVD chamber C2, a substrate heating chamber C3, a hydrogen or oxygen plasma treatment chamber C4, and a laser irradiation / application chamber C5 are respectively connected to a substrate transportation chamber C7 through gate valves GV1 to GV6 (GV6 is a reserve). Each process chamber possesses gas introduction devices gas1 to gas7 and vents vent1 to vent7. Treatment substrates sub2 and sub6 which are introduced from the load / unload chamber are transported to each process room by a transportation robot which is comprised in the substrate transportation room. In the laser irradiation / application chamber C5, after a liquid thin film pattern is formed by an applying means which is not illustrated, it is heated and solidified. Next, laser light which is supplied through one or both of a first beam line L1 and a second beam line L2 is formed by laser synthesis optical devices opt1, opt2, and it is applied to a surface of the substrate through a laser introduction window Wl.

[0025] Since the substrate can be prevented from exposure to the atmosphere by using the above mentioned device, in the case of manufacturing such as a laminated structure with a plasma CVD SiO_2 film, a clean interface can be formed.

[0026] With reference to Figs. 5(a) to 5(d), the second embodiment is explained. The droplet 102 is fiied and adhered onto the substrate 101 (the same figure (a)) and then the liquid pattern 503 is formed (the same figure (b)). The pattern size and the film thickness are controlled by the unit quantity and the number of the droplets which are

flied and adhered. A desired liquid pattern 504 is formed on the surface of the substrate 101 by transferring a droplet discharge means relatively to the substrate or transferring the substrate 101 relatively to the droplet discharge means. At this time, when the pattern size and the film thickness are controlled, a parameter is set sufficiently considering the viscosity of the droplet, the surface tension over the substrate, the size of an island-like film to be formed, and the like. Here, a film whose film thickness is thicker than the desired film thickness, or as shown in Fig. 5(b), in the case where an irregularity is formed on the top surface in a cross-sectional shape when the pattern 504 is solidified, a flattening step of the surface is performed. The flattering step, as shown in Fig. 5(c), is performed by forming the oxide film 505 in the upper part, and subsequently, polishing and removing the surface of the solidified pattern 504 and the oxide film at the same time by a chemical mechanical polishing method. In addition, the laser 105 may be applied to the entire or a part of the substrate, as necessary. As the flattering means, an etching by a chemical, a mechanical polishing method, and an ion milling method, and the like is selected depending on the material.

[0027] Next, with reference to Figs. 6 and Fig. 7, the third embodiment of the present invention is explained. Figs. 6(a) to 6(d) each show respectively a part of the forming steps of the thin film transistor. A thin film pattern 604 is formed by applying a liquid raw material in an island-like shape over the substrate 101 on which a suitable substrate covering film is deposited (the same figure (a)). Next, a crystalline silicon film 605 is formed through a heating / solidifying step at 300 °C and a laser recrystallization step (the same figure (b)). Subsequently, a trisilane ($Si3H_8$) film 606 which is a liquid raw material is formed by a spin coating method (the same figure (c)). A spinning

condition is set to obtain a desired film thickness. After finishing the coating, annealing is performed at 600 °C under a reduced pressure oxygen atmosphere. By carrying out like this, the trisilane is oxidized and an oxide film 607 is formed (the same figure (d)). Hereby, a crystallized silicon film pattern 605 which is covered by the oxide film 607 is formed. Next, the thin film transistor is formed through forming the gate electrode, injecting an impurity in a source/drain region, annealing, forming a wiring metal, and the like.

[0028] Fig. 7 is a schematic cross-sectional view of the device to form the oxide film positively. Power is supplied to a high frequency electrode RF2 from a high frequency power source RF1 (a high frequency of 13.56 MHz or more is suitable). Plasma is formed between an electrode with a gas supply hole RF3 and the high frequency electrode, and then a radical which is formed by reaction is led through the electrode with a gas supply hole to a region where the substrate is arranged. An oxygen radical is supplied to the surface of the substrate sub2 by using a gas which contains oxygen as a material gas. At this time, other gas may be introduced without exposing it to the plasma by a flat type gas introduction device RF4, and it is also possible to form a silicon oxide film by introducing silane or the like. Thus, an oxide film formation device is, as shown in the same figure, provided with the vent ven2, the gas introduction device gas2, an oxygen line gas21, a helium line gas22, a hydrogen line gas23, a silane line gas24, a helium line gas25 and an argon line gas26. It is possible to heat a substrate holder S2 up to from a room temperature to about 500 °C by a heater or the like. As a configuration of the above mentioned oxygen radical supplying device, it is possible to use not only the above mentioned parallel flat plate RF plasma CVD device, but also the method which does not use the plasma such as a reduced pressure CVD and

a normal pressure CVD, and the plasma CVD device which uses a microwave and an ECR (Electron Cyclotron Resonance) effect. Furthermore, it is also possible to form a nitride film by using the raw material which contains a nitrogen instead of the oxide.

[0029] In addition, the above mentioned method is possible for the following application since it is suitable for forming a highly pure thick oxide film of 1 μm or more. The glass substrate over which an active-matrix liquid crystal display which used the thin film transistor and an image sensor is formed contains a minute amount of an alkali metal, and the like. In an annealing step and a laser crystallization step, a substrate cover layer is used in order to prevent the impurity such as the alkali metal from diffusing from the substrate to an active layer silicon, an insulating film and its interface, and it is suitable for a method for forming the silicon oxide film for the cover layer. A process time can be shortened compared with deposition by a conventional CVD method and the like. On the other hand, an interlayer insulating film which is used in a semiconductor process, an active-matrix TFT-LCD, and the like is often required to have a planarity of the upper part. In such application, since a flat surface is formed by coating with a liquid raw material, it becomes an excellent alternative means.

[0030] As mentioned above, the present invention is explained based on a suitable embodiment, and a method for forming the thin film of the present invention is not limited only to a the structure of the above mentioned embodiments, and a method in which various corrections and modifications from the construction of the above mentioned embodiments are made also included in a scope of the present invention.

[0031]

[Effect of the Invention] According to a method for forming a thin film of the present

invention, since a thin film pattern can be formed by selectively supplying a raw material which has fluidity over a substrate, the number of manufacturing steps can be reduced by omitting a photolithography step and an etching step, and reduction in the amount of the raw material to be used can be realized. Furthermore, as for a silicon based thin film, formation of a highly efficient semiconductor element at a low cost can be realized by applying an oxidation technique of a coating film to an insulating thin film which is formed by a method for forming a thin film of the present invention.

[Brief Description of Drawings]

[Fig. 1] A sectional view of every step, which shows a method for forming a thin film according to the first embodiment of the present invention sequentially.

[Fig.2] (a) and (b) are a sectional view which shows a structure of a single body of a discharge device and a perspective view which shows a structure of the discharge device which is arranged in the shape of an array, respectively.

[Fig.3] A schematic plan view of a liquid pattern formation device which is used in the present invention method.

[Fig.4] A plan view of a complex device which includes the liquid pattern formation device which is used in the present invention method.

[Fig.5] A sectional view which shows a method for forming the thin film according to the second embodiment of the present invention sequentially.

[Fig.6] A sectional view which shows a method for forming the thin film according to the third embodiment of the present invention sequentially.

[Fig.7] A schematic cross-sectional view of an oxygen radical supplying device which is used in the third embodiment.

[Description of Notations]

101: substrate

102: droplet

103: liquid pattern

104: solidified pattern

105: laser

106: crystallized film

201: nozzle

202: heater

203: discharge port

204: supply port

205: drive circuit substrate

206: drive circuit

207: supply means

208: control means

301: laser oscillator

302: optical element

303: transfer means

304: optical path

305: transportation room

306: gate valve

307: laser introduction window

308: discharge device

309: process chamber

310: vent

311: substrate stage

312: vent

504: thin film pattern

604: liquid pattern

605: thin film pattern

606: trisilane film

607: oxide film